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This project was devoted to evaluating the phase chemistry and thermochemistry of the quaternary lead-magnesium-niobium titanate system (PbO-MgO-Nb$_2$O$_5$-TiO$_2$). It is technologically relevant to the development of ferroelectric relaxors with the perovskite crystal structure and of the general composition Pb(Mg$_{0.33-0.33x}$Nb$_{0.67-0.67x}$Ti$_x$)O. This project also evaluated the phase chemistry of most of the remaining compositions of the system. The four ternary phase diagrams of PbO-MgO-Nb$_2$O$_5$, PbO-MgO-TiO$_2$, PbO-Nb$_2$O$_5$-TiO$_2$ and MgO-Nb$_2$O$_5$-TiO$_2$ at 1000°C were determined in some detail. The quaternary phase diagram was evaluated for relatively PbO-poor compositions. In addition, the thermochemistry of the overall system was also evaluated between about 800 and 1000°C, characterized in the form of equilibrium vaporization rates of lead oxides. This was accomplished by Knudsen cell gravimetry on binary, ternary and quaternary phase states that were thermodynamically well defined. From this, the formation thermodynamics of a number of solid phase compositions were determined for the first time. Moreover, trends were evaluated of the equilibrium vapor pressures over perovskite solid solutions as a function of composition.

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Final Report

Physical Chemistry of the PbO-MgO-Nb$_2$O$_5$-TiO$_2$ System for Ferroelectric Relaxors

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Report Summary

This is the final technical report for research devoted to evaluating the phase chemistry and thermochemistry of the quaternary chemical system PbO-MgO-Nb_2O_5-TiO_2. While greatest technological interest focuses on the chemical state surrounding the compositions of the $Pb(Mg_{0.33-0.33x}Nb_{0.67-0.67x}Ti_x)O_3$ perovskite solid solution, this project went well beyond to evaluate the phase chemistry at most of the remaining compositions. In particular, the four ternary phase diagrams of PbO-MgO-Nb_2O_5, PbO-MgO-TiO_2, PbO-Nb_2O_5-TiO_2 and MgO-Nb_2O_5-TiO_2 at 1000°C were determined in some detail. That for the latter was also evaluated at higher temperatures up to 1450°C, in order to help with the interpretation of the chemical complexities discovered at lower temperatures. The quaternary phase diagram was evaluated in general form for relatively PbO-poor compositions. However, significant attention was given to determine the range near chemical states near the perovskite composition of $x = 0.32$ that is important for the manufacturing of ferroelectric relaxors.

The thermochemistry of the overall system was also evaluated between about 800 and 1000°C, characterized in the form of equilibrium vaporization rates of lead oxides. This was accomplished by Knudsen cell gravimetry on binary, ternary and quaternary phase states that were thermodynamically well defined. From this, the formation thermodynamics of a number of solid phase compositions were determined for the first time. What is perhaps more important, the equilibrium vaporization rates were determined for the perovskite solid solution, as a function of the solid composition and temperature. This is of greatest value to those researchers who are concerned about controlling composition while synthesizing single crystals and polycrystalline ceramic forms of the ferroelectric relaxors.

One scientific innovation of this project was the development of an effective method for evaluating the solid state thermodynamics of lead-bearing electroceramics. In this study, thermodynamic results were summarized graphically in the form of plots of lead oxide activity as a function of the relative cation fractions of the remaining metal components, namely, Mg, Nb, and Ti. For most other chemical systems, thermodynamic activity is determined directly by measuring equilibrium vapor pressure of a simple vapor species in equilibrium with a condensed phase and then comparing it to the vapor pressure of a standard state. However, the molecular distribution of lead oxides in the gas phase is quite complex, with several molecular species simultaneously coexisting at significant concentrations. Consequently, the interpretation of gravimetric measurements requires some care.

This forced the development of a new calibration scheme based on chemical systems that have already been well characterized thermodynamically via independent experimental methods. We used pure lead oxide and the two, two-phase equilibria of $PbZrO_3ZrO_2$ and $PbTiO_3TiO_2$ as calibrants since they have already been carefully examined by solid state electrochemistry and other means. This allowed us to construct calibration plots of weight loss rates vs. thermodynamic activity for each temperature. While there are refinements to be made to this method, it clearly provides a viable method for measuring the thermodynamics of other lead oxide systems that by-passes the problems that currently plague other techniques.

Aside from the technological value of the phase diagrams and vapor pressure measurements, there were several interesting scientific findings of this project. One discovery is what seems to be a general rule on the substitutional compatibility of Ti^{4+} cations for the cationic combination of $(Mg_{1/3}Nb_{2/3})^{4+}$ in a wide range of crystal structures. This gives rise to highly specific compositions that range widely in one compositional direction, but very narrow in another. The effect is that several crystal structures, of nominally different lattice stoichiometries exhibit parallel compositional paths. This is particularly evident in the $MgO-Nb_2O_5-TiO_2$ system. This observation reveals a particularly valuable chemical system with which to advance or test new rules of crystal chemistry.

Another important finding concerns the chemical relationships of the pyrochlore phase relative to the technologically desirable perovskite phase. Somewhat of a mystery before this project, it is now clear that the pyrochlore phase dominates the phase diagram as being one of the most stable phases, at least with respect to the range of lead oxide activities for which it exists. This explains why it frequently appears as an impurity in so many recipes attempting to make the pure ferroelectric compound. As such, this project has demonstrated that simultaneously maintaining both a high activity of lead oxide and a slight excess of MgO is one method for avoiding the pyrochlore phase in high temperature equilibrium phase assemblages.

Finally, this project undertook the task of examining schemes for controlling the vapor pressure of lead oxide at high temperature. The objective was to develop a scheme that was both compact in dimensions but capable of maintaining a constant vapor pressure and self correcting if, for some reason, experimental conditions changed within the annealing chamber where the perovskite phase was being synthesized. After considering a few possibilities, the scheme chosen for closer scrutiny was that of an electrochemical pump based on liquid electrolytes and separate electrodes of liquid lead and oxygen gas. Constructed much like a free energy cell for measuring the Gibbs energies of liquid lead oxide compounds, the principal was to impose a set voltage on the electrochemical cell, thereby ensuring that the chemical potential of lead oxide was maintained at a prescribed level. Gas phase exchange at the electrolyte surface would therefore moderate the vapor pressure of the lead oxide. After some experimentation, our conclusion is that the principal of scheme is sound, however, the application of the device is severely complicated by several corrosive interfaces, which are conducting electrolytic current that unduly limits the lifetime of the experimental cells.

Introduction

This was project that formally received three formal years of funding. The first two years were conducted as a collaboration, subcontracted from the National Institutes of Standards and Testing. The principal investigator at NIST was by Dr. John Blendell who also served as the project's technical manager. The primary grant from AFOSR was in response to the original proposal entitled "Grain Growth in Relaxor Ferroelectrics" (AFOSR ISSA-99-0013; 12/1/99 to 12/31/01). The third year of funding was split off from the NIST collaboration and directly received from AFOSR under this grant issued directly to the Arizona State University (entitled "Physical Chemistry of the PbO-MgO-Nb_2O_5-TiO_2 System for Ferroelectric Relaxors"; AFOSR Grant Award #: F49620-02-1-

0144). As such, this report is a summary for the full project as it was technically conceived.

The following report first summarizes the technical accomplishments of this project followed by additional details of activities to disseminate the information gained. In addition to publications, oral presentations and reports, this project funded the dissertation work of one doctoral candidate, plus provided opportunities for several undergraduate students and post doctoral research associates to conduct high level, high quality research that has enriched their scientific training.

Acknowledgements

Technical Results

(a) Equilibrium Phase Chemistry of the PbO-MgO-Nb_2O_5-TiO_2 System

The tetrahedral axes shown in Fig. 1 illustrate the compositional framework for the quaternary PbO-MgO-Nb_2O_5-TiO_2 system. The four outside faces of the tetrahedron represent the quasi-ternary compositional systems PbO-MgO-Nb_2O_5, PbO-TiO_2-Nb_2O_5, PbO-MgO-TiO_2 and MgO-TiO_2-Nb_2O_5. The phase chemistry for each has been determined experimentally at 1000°C and is shown in Fig. 2. With respect to ferroelectric relaxors, the technologically important perovskite compositions lies on the PMN-PT join shown in Fig. 1 that cuts through the interior of the tetrahedral solid. Lead titanate ($PbTiO_3$) is located at one end and the $Pb(Mg_{1/3}Nb_{2/3})O_3$ at the other of this perovskite solid solution. These compositions are coplanar with the PbO-TiO_2-$MgNb_2O_6$ pseudo ternary section shown in transparent shading. On the base is shown the PbO-MgO-Nb_2O_5 phase diagram for contextual orientation.

The experimental method of determination of each diagram was determined primarily by high temperature annealing of mixtures of powdered oxides formulated in a series of strategic compositions intended to elucidate individual features. A variety of experimental procedures were employed to ensure that the
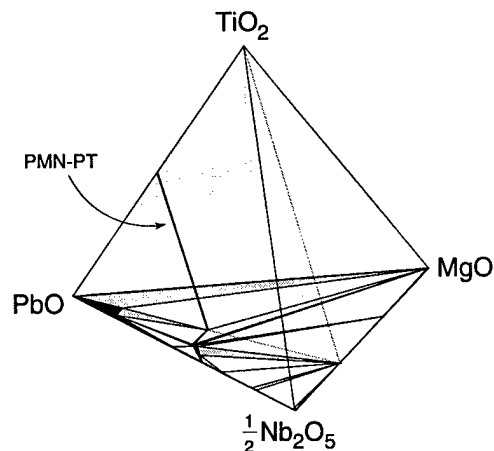

Fig. 1. Quaternary axes of PbO - MgO - Nb_2O_5 - TiO_2 system illustrating the pseudo-ternary plane containing the perovskite solution PMN-PT. The
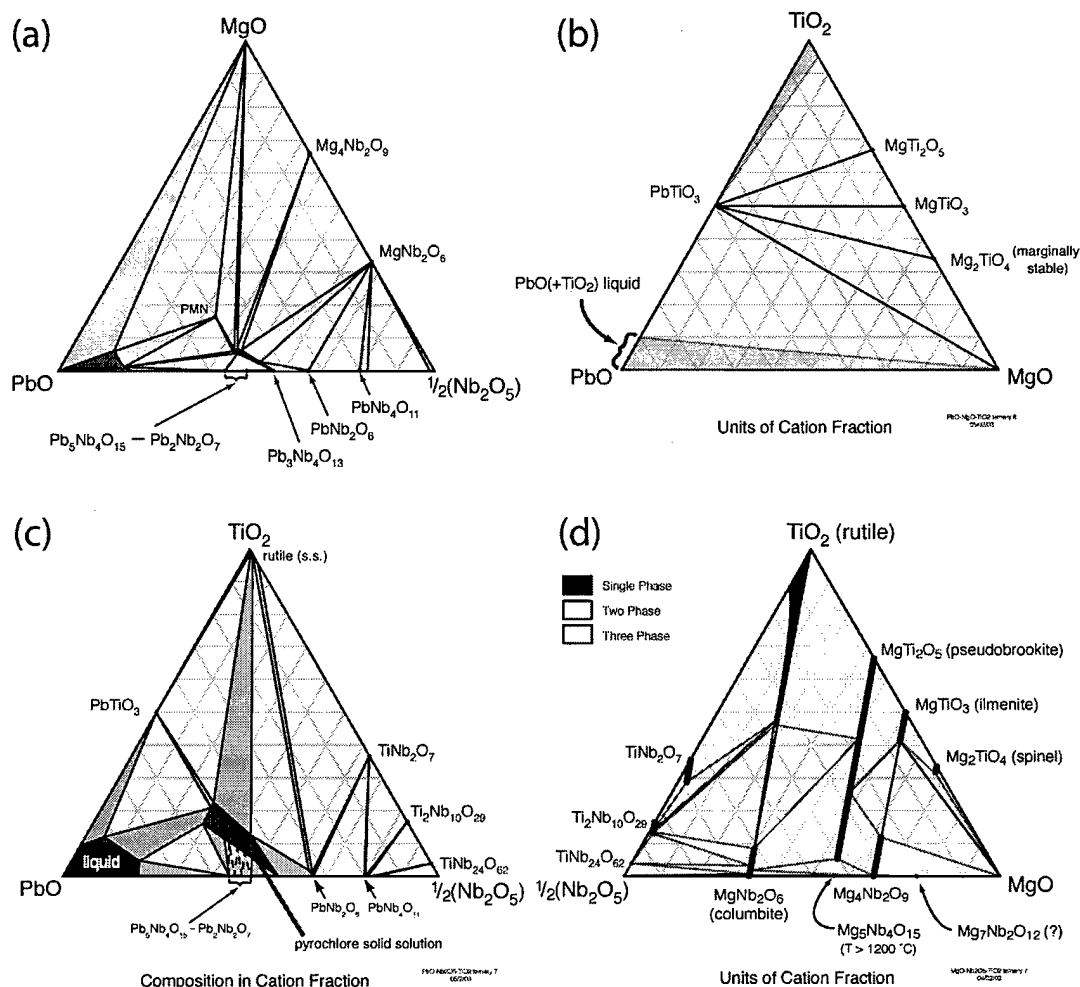
Fig. 2. Experimentally determined ternary phase diagrams of the PbO-MgO-Nb$_2$O$_5$-TiO$_2$ system at 1000°C[1,2].

information portrayed at 1000°C was accurately conveyed. In some cases, particularly for the MgO-TiO$_2$-Nb$_2$O$_5$ system, this meant that certain equilibria were probed at higher temperatures and the behavior extrapolated to 1000°C. This was because of sluggish diffusion for compositions that contained little or no lead oxide.

The phase diagram for the PbO-MgO-Nb$_2$O$_5$ system shown in Fig. 2a is essentially complete except for the small region just to the PbO-rich side of the pyrochlore phase marked by Pb$_3$Nb$_4$O$_{13}$ at one vertex. A particularly important feature of this diagram is the relationship of the pyrochlore phase with the other phases. Effectively, the pyrochlore dominates the system by equilibrating with every other compound except the two lead-poor phases PbNb$_2$O$_6$ and PbNb$_4$O$_{11}$. This explains the persistence of the pyrochlore appearing in most attempts to synthesize the pure

$Pb(Mg_{1/3}Nb_{2/3})O_3$ ferroelectric phase. This diagram offers the strategy to avoid the pyrochlore by maintaining slight excesses of MgO and PbO in the system.

The only information missing from Fig. 2a centers on the narrow compositional region between $Pb_5Nb_4O_{15}$ and $Pb_2Nb_2O_7$. This involves several phases that equilibrate with the pyrochlore, but otherwise do not factor into the chemistry of the PMN perovskite.

The phase diagram of the $PbO-MgO-TiO_2$ shown in Fig. 2b is deceptively simple. Accurate experimental determination of the solubility limit of TiO_2 in liquid PbO was often obscured by the complex microstructures to have evolved upon quenching of the liquid. An additional complexity was the fact that the compound Mg_2TiO_4 is unstable below about 1000°C. This compound is entropically stabilized at high temperatures due to the cation mixing of Mg^{2+} and Ti^{4+} on their respective lattice sites. The interpretation of the quenched samples often depended on the precision of the temperature controller and the quench rate. In the end, the diagram shown was confirmed by thermodynamic calculations using independent data and new thermodynamic model of the liquid phase solution.

The experimentally determined, 1000°C section of the $PbO-TiO_2-Nb_2O_5$ phase diagram is shown in Fig. 2c. Like the diagram in Fig. 2a, the pyrochlore phase dominates the phase chemistry for most of the diagram. That is to say that the pyrochlore equilibrates with nearly every other phase of the system. The exceptions are those phases at the Nb_2O_5 richest corner. The shape of the pyrochlore phase field also indicates that the substitutional chemistry of the cations on the two different sites is rather complex. To accommodate the range of cation stoichiometries indicated, it is necessary for the cation and anion vacancies to accommodate the variation of the overall cation valences. This behavior was also seen for the pyrochlore phase in the $PbO-MgO-Nb_2O_5$ system, although to a much lesser extent.

The final external ternary phase diagram is that of the $MgO-Nb_2O_5-TiO_2$ system shown in Fig. 2d for the 1000°C isothermal section. This was largely deduced by extrapolations of trends from the experimentally determined phase diagrams for 1250°C, 1350°C and 1450°C. This was necessary because of the sluggish diffusion for certain composition ranges. The most striking feature is the parallel compositional alignment of several solid solutions, particularly with respect to the rutile, columbite, psuedobrookite, and ilmenite crystal structures. To a lesser extent, this behavior was seen for the spinel and titanium-rich phases. This feature could be explained by the same substitutional pattern of the cations, whereby $1/3(MgNb_2)^{4+}$ replaced Ti^{4+} on octahedral sites. In the rutile (TiO_2) phase, up to 79 cation % of Ti^{4+} could be replaced with the Mg/Nb combination.

An additional feature of these solid solutions was the consistent observation of miscibility gaps within this mixing scheme. The three magnesium titanate phases are already known to be entropically stabilized at higher temperatures, attributed to the mixing of Mg^{2+} and Ti^{4+}. The addition of Nb^{5+} according to the above mixing scheme then adds an additional mixing term that further stabilizes these compounds. With increasing temperature, the tendency was for the miscibility gaps to close up, Notably, the gap with respect to the pseudobrookite phase closed completely above about 1250°C. While these gaps for the other phases narrowed at high temperatures, they still persisted up to 1450°C, the highest temperature probed.
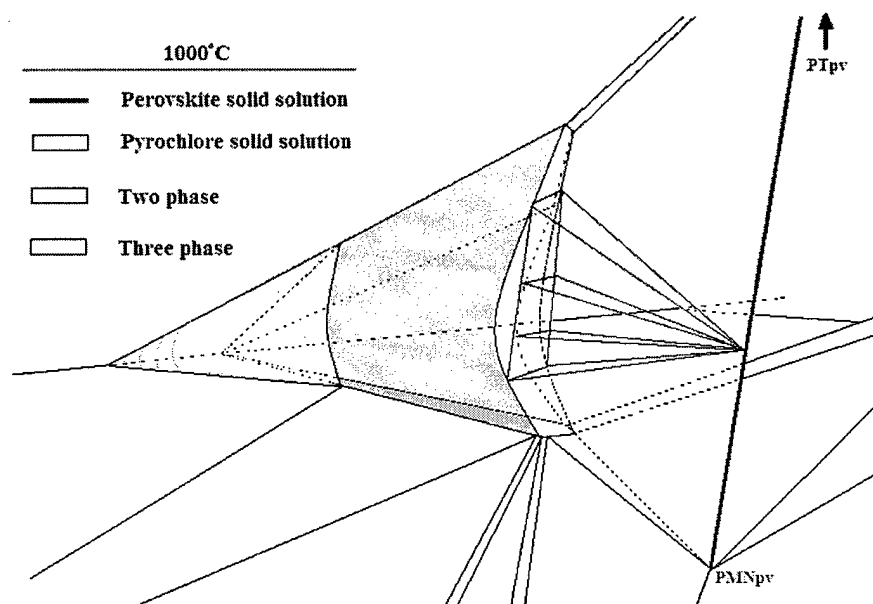
Fig. 3. Schematic of the shape and context of the pyrochlore solid solution, $Pb_{2-x}(Mg,Nb,Ti)_2O_{7-y}$, shown in gray shading, and the perovskite solid solution shown as the red line extending from its termini of $Pb(Mg_{1/3}Nb_{2/3})O_3$ (a.k.a., PMN_{pv}) and $PbTiO_3$ (a.k.a., PT_{pv}). A miscibility gap appears within the pyrochlore in equilibrium with one composition of the perovskite solid solution[1].

The cation mixing could be conveniently explained on the basis of equivalent oxidation states and the compatibility of octahedral bond lengths. As calculated from bond valence formulae, the ideal bond lengths for the cations in octahedral coordination with oxygen are Mg-O = 2.099 Å, Nb-O = 1.978 Å, Ti-O = 1.965 Å). The resultant volume change in replacing a Ti^{4+} cation with the average $1/3(MgNb_2)^{4+}$ cation is about 8%.

Finally, the interior of the quaternary $PbO-MgO-Nb_2O_5-TiO_2$ phase diagram was probed. The illustration of this is quite complicated, requiring over the full range of compositions. An example is shown in Fig. 3, which displays one of the more important findings of this project that begins to address the complexity of the pyrochlore phase coexisting with the perovskite phase. This figure shows that the pyrochlore phase exhibits a ternary miscibility gap when magnesium and titanium are added. As such, it is possible that for one composition of the perovskite phase to equilibrate simultaneously with two pyrochlore phases, one being magnesium-rich and the other titanium-rich. The remaining perovskite solid solution compositions would equilibrate with a single pyrochlore phase that is either magnesium- or titanium-rich. This observation helps to explain some of the confusing observations that have emerged in the literature concerning the coexistence of these two crystal structures.

A fuller description of the phase equilibrium relationships within the quaternary system is given elsewhere[1]. This study accomplished characterizing the general features although there are many other details that are needed for a fuller description of the of the system.

(b)   Vapor Pressure of Lead Oxides and Compound Thermodynamics

One of the major contributions of this study has been to evaluate the equilibrium vapor properties of the $PbO-MgO-Nb_2O_5-TiO_2$ as a function of composition and the temperatures between 800 to 1000°C. The purpose of this work was to assess the stability range of the perovskite phase with respect to lead oxide vapor pressure; and, thereby, provide information for evaluating the formation thermodynamics of a number of lead-bearing compounds. Of course, the emphasis has been on the perovskite phase and the compounds immediately surrounding it in composition space, but the analysis was extended to other parts of the system.

There were complexities in this analysis because of the multiple molecular species that lead oxide could exist in the gas phase at equilibrium. While there have been mass spectrometric studies in the past on the equilibrium gas phase speciation of lead oxide, different literature results disagreed with one another. Moreover, it seemed that all did not agree with gravimetric analyses. Consequently, this project bypassed this problem by inventing a calibration procedure based upon known lead compound phases that had already been thermodynamically evaluated by independent experimental means. This procedure was used to identify the best molecular model in the gas phase, although it has to be acknowledged that the agreement is fair, but not good. Therefore, this thermodynamic study relied more on its calibration procedure to provide an assessment of the thermodynamic activity of PbO, rather than explicitly attempt to evaluate the gas phased molecular distribution.

In the end, the most useful information for technologists interested in controlling composition of ferroelectric relaxor materials at high temperatures is actually the rates of vaporization. This is characterized by the Knudsen effusion rates, from which such important parameters as Langmuir vaporization behavior can be deduced. This is precise the information obtained from this study.

Knudsen cell studies

The Knudsen effusion method for determining vapor pressures, or rather equilibrium parameters for vaporization rely on the equilibration of a gas phase with a solid inside a closed volume. The vapor pressure inside is determined by monitoring the escape of vapor through a small orifice in the cell wall. While there are several methods for determining the rate of escape from the Knudsen chamber, the most common is measuring the weight loss rate, as might be accomplished using a highly accurate thermal balance, or by mass spectroscopic evaluation. For this study, we chose gravimetric analysis because it is an absolute measurement that avoided some significant problems with mass spectrometry.

The difficulty with mass spectrometry is the ionization processes used is sufficiently violent that it partially fragments the molecular species, and thereby altering the result that was sought. There have been several such studies on pure PbO, $PbZrO_3$ and $PbTiO_3$, but the results typically disagreed with the electrochemical measurements that are considered to be highly accurate. Moreover, if mass spectrometric results were unambiguously correct, they should agree with the gravimetric results. Unfortunately, we were unable to find such confirmation. Therefore, we developed our own methodology to calibrate our measurements.

In this section, the results of our studies are presented. A discussion of our methodology and the particular issues of in making accurate measurements on lead oxide compounds are discussed in Appendix I.

Suffice it to say that the vaporization rate as measured by weight loss rate can be correlated with the thermodynamic activity of PbO. Typically, we used single phase PbO and the two, two-phase equilibria of $PbZrO_3ZrO_2$ and $PbTiO_3$-TiO_2 as our thermodynamic standards. Figure 4 presents a calibration curve for 1000°C that plots the weight loss rate measured in our study as a function of the lead oxide activity for these equilibria. The activity for pure liquid lead oxide was accepted as the standard state,
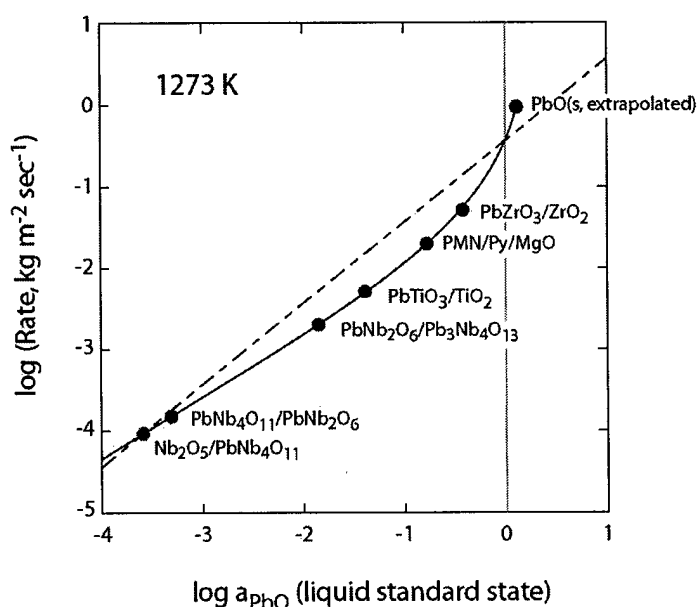

Fig. 4. Knudsen effusion rate from various vapor-condensed phase equilibria as a function of lead oxide activity (liquid lead standard state). Black points correspond to points calibrated using thermodynamic data derived from published electrochemical studies. The curve was derived form gas phase molecular distribution model from Drowart, et al[1,3], corrected by a single additive parameter to fit this data. Red points correspond to some of the equilibria of the PbO-MgO-Nb_2O_5-TiO_2 system examined in this study. Dashed line correlates with the case assuming that monomolecular PbO was the only

therefore, a_{PbO} = 1 by definition. The activity of lead for the two, two-phase equilibria were determined from published electrochemical measurements. In Fig. 4, the black points correspond to the calibration points. The curve corresponds to a model modified from the gas phase molecular distribution that most closely matched our results. (In this case, the work of Drowart, et al[3] was considered must descriptive, although their results required a single correction term applied over the entire range of activities to bring it into accordance with our experimental results.)

Figure 5 presents the weight loss rates as a function of temperature due to Knudsen effusion from a selection of equilibria in the PbO-MgO-Nb_2O_5 system. Note that the equilibrium for the $Pb(Mg_{1/3}Nb_{2/3})O_3$-pyrochlore-MgO equilibrium lies between those of the $PbZrO_3ZrO_2$ and $PbTiO_3TiO_2$ equilibria. Effectively, this points out the greater stability of lead titanate relative to the PMN perovskite, and further indicates the range of equilibrium vapor pressures for the perovskite solid solution.

The vaporization rates of these various equilibria at 1000°C are again plotted in Fig. 4, indicated by the red dots. Knowing the vaporization rates, the corresponding
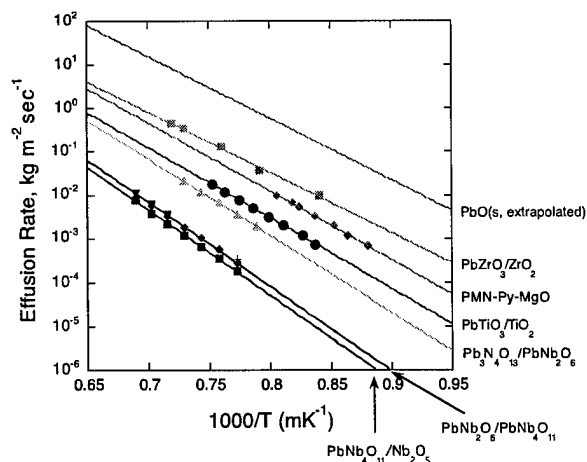
Fig. 5. Equilibrium effusion rates as a function of temperature of selected equilibria within the PbO-MgO-Nb$_2$O$_5$-TiO$_2$ system[1].

equilibrium activity of lead oxide can be determined from the calibration curve. The accuracy of the lead oxide activities will be greatest for the PMN-pyrochlore-MgO equilibrium since it resides inside the calibration points provided by the PbZrO$_3$ZrO$_2$ and PbTiO$_3$TiO$_2$ equilibria. At lower lead oxide activities, there are no calibration points in which to assess the accuracy of the thermodynamic model adopted. As such, it can be expected that the activities so determined in this range will have greater errors.

All of this thermodynamic information can be combined in what is referred to as a phase stability diagram. This is a diagram that maps out the range of stability of phases as a function of the lead oxide activity and relative composition of the remaining cations. Figure 6 displays the diagram for the PbO-MgO-Nb$_2$O$_5$ system. The horizontal axis corresponds to the relative cation fraction of Mg and Nb, whereas the lead content is represented by chemical potential (in this case $\log a_{PbO} = \Delta\mu_{PbO}/2.303RT$) along the vertical scale. (For clarity, the vertical axis is not to scale so as to easily distinguish the different phase fields.) Within the interior of the diagram, a vertical line refers to a ternary or quaternary compound that has reasonably fixed stoichiometry with respect to Mg/Nb content. The large phase field marked "Py" corresponds to the homogeneity range of the pyrochlore phase, which seems to dominate the stability range of the diagram at higher PbO activities. Most important is the limited stability range

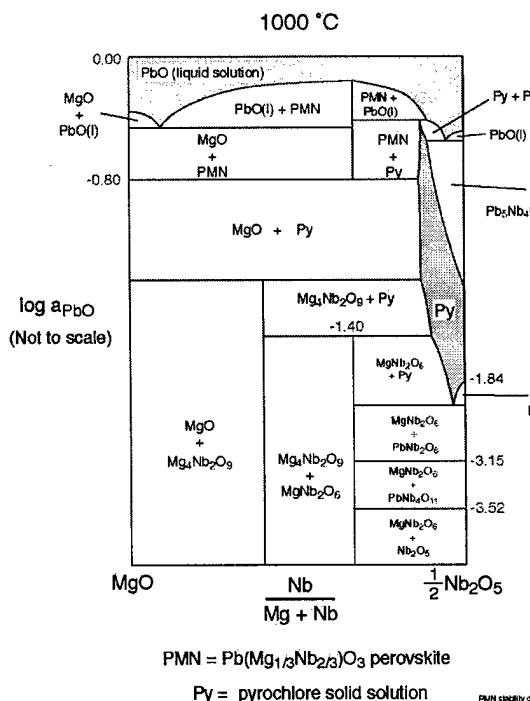PMN = Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ perovskite
Py = pyrochlore solid solution

Fig. 6. Stability diagram for the PbO-MgO -Nb$_2$O$_5$ system at 1000°C

of the perovskite phase near the top of the diagram, at 0.67 on the horizontal scale. It is clear that the perovskite phase has both an upper and lower limit of stability relative to PbO activity. As experimental observed by others, the loss of PbO converts the perovskite to the pyrochlore phase, which is stable to much lower activities.

Similar stability diagrams have been generated for the PbO-MgO-TiO_2 and PbO-Nb_2O_5-TiO_2 systems. Refinement of the diagrams of all of these lead oxide bearing systems awaits the refinement of the thermodynamics of these systems. In particular, the thermodynamics of the liquid solution phase that is predominantly PbO is needed. It is clear that the perovskite phase will easily degrade to the pyrochlore at only modestly low lead oxide activities (i.e., $a_{PbO} = 0.157$). Consequently, synthesis of the ferroelectric relaxor phase must be done in a relatively rich environment of lead oxide. On the other hand, too much lead oxide as a liquid is corrosive to the perovskite phase, which will dissolve away.

Finally, Fig. 7 displays the equilibrium activity of lead oxide for the perovskite in equilibrium with MgO and the pyrochlore phase(s). The range of activities is rather modest, varying only by a factor of about 3 from one compositional extreme, $Pb(Mg_{1/3}Nb_{2/3})O_3$, to another, $PbTiO_3$. The equ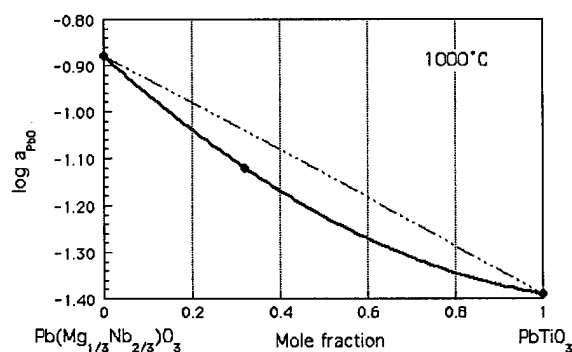ilibrium activity of PbO for the solid solution 32PT:68PMN lies slightly below the linear trend established by the end points. While it is tempting to suggest that this is an indication of negative deviation from ideal mixing, it must be kept in mind that the pyrochlore phase is also changing with composition. Moreover, phase equilibrium results indicates that there is one position along this solid solution whereby the perovskite equilibrates with two pyrochlores of different composition because of the solubility gap for titanium and magnesium rich pyrochlore compositions.

Fig. 7. Activity of lead oxide for the equilibrium of PMN-PT solid solution in equilibrium with MgO and pyrochlore(s).

Project Participants

Personnel Supported by Grant
<u>Significant support</u>
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Project Activities: List of Reports and Presentations

<u>Publications:</u>

"Phase Equilibria in the Lead-magnesium-Niobium-Oxygen System at 1000°C,"
P. Lucas and W. T. Petuskey, *J. Am. Ceram.* Soc., 84 [9] 2150-52 (2001)

"The High-Temperature Phase Chemistry and Thermochemistry of the lead
Magnesium Niobium Titanium Oxide System," Robert I. Mangham, Ph.D.
Dissertation, Arizona State University, Department of Chemistry & Biochemistry,
May, 2003.

"High Temperature Phase Equilibria of the Magnesium-Niobium-Titanate
System," Robert I. Mangham and William T. Petuskey, *J. Am. Ceram. Soc.*
(submitted)

"Phase Equilibria of the Lead-Magnesium-Titanate, and Lead-Niobium-Titanate
Systems at 1000 C and 1atm," Robert Mangham and William T. Petuskey, (in
preparation)

"Phase Equilibria of the Quaternary System $PbO-MgO-Nb_2O_5-TiO_2$," Robert
Mangham and William T. Petuskey, (in preparation)

"Thermodynamic Analysis of PbO-based Ceramics by Knudsen Cell
Gravimetry," Robert Mangham and William T. Petuskey, (planned)

"Equilibrium Vapor Pressure Behavior of the $PbO-MgO-Nb_2O_5$ and PbO-MgO-
Nb_2O_5 Systems," Robert Mangham and William T. Petuskey, (planned)

"Thermodynamics and Vapor Pressure behavior of PMN-PT Perovskites from Knudsen Cell Gravimetry," Shuling Guo, Robert Mangham and William T. Petuskey, (planned).

Written reports:

Interim Report #1, "Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System", for the period 12/1/99 to 3/31/00, submitted to NIST June 19, 2000.

Interim Report #2, "Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System", for the period 4/1/00 to 9/30/00, submitted to NIST November 22, 2000.

"Phase Diagram Studies of PMN-PT," W. T. Petuskey, extended abstract based on oral presentation given at the AFOSR Contractor's Meeting on Ceramic Materials & Composites, Saint Louis, May 4-5, 2000.

Interim Report #4, "Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System", for the period 4/1/01 to 6/30/01, submitted to NIST October 23, 2001.

"Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System," W. T. Petuskey, proceedings of the Joint Metallic & Ceramic Materials Programs Review, AFOSR, Snowbird, Utah, August 19-21, 2001, distributed on compact disk.

Interim Report #5, "Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System", for the period 6/1/01 to 9/30/01, submitted to NIST January 17, 2002.

Final Report, "Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System", includes progress report for the period 10/1/01 to 12/31/01, submitted to NIST June 17, 2002.Interim Report #1, "Phase Chemistry and General Thermochemistry of the PbO-PMN-PbTiO$_3$ System", for the period 12/1/99 to 3/31/00, submitted to NIST June 19, 2000.

"Physical Chemistry of the PbO-MgO-Nb$_2$O$_5$-TiO$_2$ System for Ferroelectric Relaxors," W. T. Petuskey, Joint 2002 Contractors Meeting in Metallic materials and Ceramic Materials, AFOSR/AFRL FY02, Bar Harbor, Maine, August 12-14, 2002.

<u>Oral Presentations:</u>

"Grain Growth in Ferroelectric Relaxors", J. Blendell, J. Wallace, C. Handwerker, W. T. Petuskey, presented at the Piezocrystals Workshop, sponsored by DARPA, in Herndon, VA, January 19-20, 2000.

"Phase Chemistry – Crystal Chemistry Involving PMN Perovskites," W. T. Petuskey, paper A2-064-00 presented at the 102nd Annual Meeting of the American Ceramic Society, in St. Louis, April 30-May 3, 2000.

"Phase Diagram Studies of PMN-PT," W. T. Petuskey, AFOSR Contractor's Meeting on Ceramic Materials & Composites, Saint Louis, May 4-5, 2000.

"Phase Chemistry & Thermodynamics of the PbO-PMN-PT System," presented at the joint AFOSR/DARPA review on the Solid State Crystal Growth of Ferroelectric Relaxors program in Arlington, VA, April 18, 2001.

"Phase Chemistry and Thermochemistry of the $PbO-PMN-PbTiO_3$ System," Robert Mangham and William T. Petuskey, poster presentation at the Joint Metallic & Ceramic Materials Programs Review, AFOSR, Snowbird, Utah, August 19-21, 2001.

"Vapor Pressure Measurements by Knudsen Cell Gravimetry," W. T. Petuskey, presented at the Arizona State University - Bruker Optics - Netzsch STA / Evolved Gas Analysis Workshop, Tempe, Arizona, August 15-17, 2001.

"Phase Chemistry of the $PbO-MgO-Nb_2O_5-TiO_2$ System," R. Mangham and W. T. Petuskey, presentation AMH.1-C-09-2002 given at the 104th Annual Meeting of the American Ceramic Society, St. Louis, MO, April 30, 2002.

"PbO Activities in the $PbO-MgO-Nb_2O_5-TiO_2$ System Measured by Knudsen Cell Gravimetry and Liquid Metal Probes," R. Mangham and W. T. Petuskey, presentation (AMH.1-C-10-2002) given at the 104th Annual Meeting of the American Ceramic Society, St. Louis, MO, April 30, 2002.

"Applying Concepts of Bond Valence for Describing Structural Trends of Perovskites," William T. Petuskey and George H. Wolf, poster presentation (D4.18), symposium D (Perovskite Materials), Spring Meeting of the Materials Research Society, San Francisco, 4/2/02.

"Systematics in the Phase Chemistry and Thermo- Chemistry of Lead Oxide-Based Perovskites," W. T. Petuskey, R. Mangham, P. Majhi, C. Wang and S.K. Dey, presentation (D1.7) given at symposium D (Perovskite Materials), Spring Meeting of the Materials Research Society, San Francisco, 4/2/02.

"Searching for New Ceramics," W. T. Petuskey, presented at the Pacific Northwest National Laboratory, (Environmental Materials Science Laboratory), Richland, WA, May 19, 2002

"The High Temperature Physical Chemistry of PMNT Perovskites for Synthesizing Ferroelectric Relaxors," W. T. Petuskey, presented at the AFOSR/AFRL FY02 Review on Ceramics and Metals, Bar Harbor, Maine, August 12-14, 2002.

"The High Temperature Phase Chemistry and Thermochemistry of the PbO-MgO-Nb$_2$O$_5$-TiO$_2$ System," R. Mangham and W. T. Petuskey, presented at the 2003 U.S. Navy Workshop on Acoustic Transduction materials and Devices, State College, PA; May 5-7, 2003.

"Thermochemical Measurements on Electroceramics by Knudsen Cell Gravimetry," William T. Petuskey, Netzsch Thermal Analysis/Thermophysical Properties Seminar, Phoenix, AZ, January 15, 2004.

Appendix I. Knudsen Cell Methodology Applied to PbO-based Electroceramics

We have established a method for measuring the vapor pressure of lead oxide by Knudsen cell gravimetry. Figure I.1 schematically illustrates a typical cell, which is usually constructed from dense, pure MgO. The cell sits on top of a thermocouple, which, in turn, sits on a sensitive thermobalance capable of measuring weight changes of better than 1 μg. At high temperatures, lead oxide evaporates from the sample and remains contained in the open space allowed. After many collisions, it is only by chance that molecules escape out of the small orifice (about 0.3 to 1.0 mm diameter). The entire cell is placed in a moderately high vacuum (10^{-8} bar), which eliminates the possibility of gases re-entering the cell. It can be assumed that equilibrium is established between the solid and the vapor if the orifice is sufficiently small.

The rate of weight loss is correlated with the vapor pressure whereby

$$\dot{w}_{tot} = \sum_i \frac{dw_i}{dt} = -C \cdot \sum_i P_i \cdot M_i^{1/2} \tag{1}$$

and

$$C = \frac{A_o \cdot W_C}{(2\pi RT)^{1/2}} \tag{2}$$

Here, the total weight loss rate consists of the individual contributions of each molecular species present in the gas phase. Each species, i, is characterized by their partial pressure, P_i, and molecular weight, M_i. The orifice area is denoted by A_o and the Clausing geometric factor, W_C, accounts for the orifice shape. For simple cases, there is only one molecular species present in the equilibrium gas phase. In such a case, the equilibrium pressure is simply related to the total weight loss rate.

Knudsen cell gravimetry has been used in several studies in the past to evaluate the thermodynamic properties of lead oxide compounds [4-7]. The difficulty encountered in those cases has been the lack of sufficiently detailed information of the lead oxide gas phase. Those researchers were forced to make simplifying assumptions that are no longer necessary.

The gas phase equilibrium of lead oxide is somewhat complex. Fortunately, there have been several mass spectrometric studies of molecular speciation from which the relative energetics of the molecules were determined [3,8-10]. This has made it possible to reliably apply Knudsen cell gravimetry to extract thermodynamic data of the underlying solids.

There are eight primary gas species that vary in their importance depending on temperature and lead oxide activity. These include Pb, O_2, and a series of six oligimers, Pb_nO_n where n = 1, 2, ..., 6. There are a few other species that have been identified but

oriface diameters: 0.6, 1.0, 1.5 m
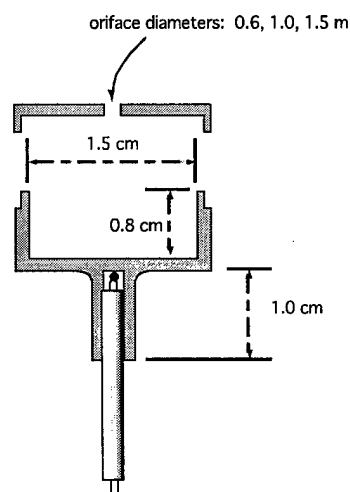
1.5 cm

0.8 cm

1.0 cm

Fig. I.1. Schematic of MgO Knudsen cell used for PbO vapor pressure measurements.

are of little consequence for the conditions of these analyses. On a log-log scale, Fig. I.2 plots the vapor pressures of these species at 1000 °C over a range of the lead oxide. These were calculated using available thermodynamic data. A critical feature is that the partial pressures of many of the species exhibit quite different dependences on a_{PbO}. This means that Knudsen cell measurements of weight loss rates can not be used directly to determine lead oxide activities but requires a more sophisticated approach that combines
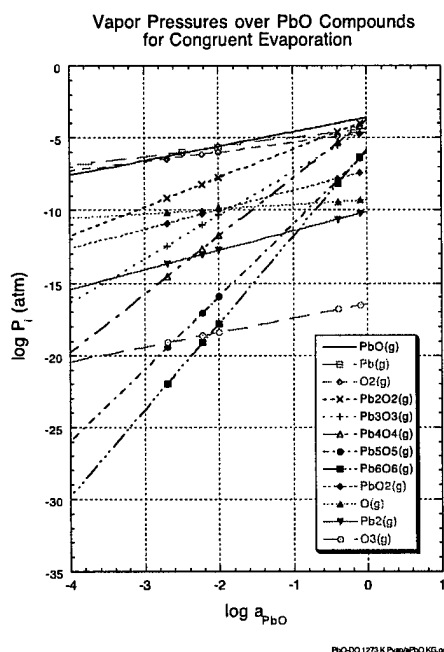

Fig. I.2. Partial pressures of different molecular species in PbO vapor as a function of thermodynamic activity of lead oxide. Corresponds to cases of congruent vaporization of PbO.

the acquired data and calculation of the gas phase thermodynamics.

The situation is made more complex because the molecular masses of the species differ considerably, ranging from 32 for O_2 to 1339 for Pb_6O_6. This affects the average molecular velocities and collision frequencies of the molecules and therefore their probability of escape from the Knudsen cell. This is accounted for by the square root dependence of the molecular masses given in Eq. (1).

Despite these complexities, knowledge of the thermodynamics of the gas phase and of the physics of Knudsen effusion allows for the determination of lead oxide activity from the weight loss rate although the equations are more complex than for cases of monomolecular gases. An expansion of Eq. (1) gives

$$\dot{w}_{tot} = -C\left[P_{Pb} \cdot M_{Pb}^{1/2} + P_{O_2} \cdot M_{O_2}^{1/2} + \sum_{n=1}^{6} P_{Pb_nO_n} \cdot M_{Pb_nO_n}^{1/2}\right] \tag{3}$$

Each of the partial pressures given in Eq. (3) can be expressed as singular functions of the activity of a_{PbO} using gas phase thermodynamics, mass action relationships between molecular species and stoichiometric restrictions of effusion of lead and oxygen from the cell. From this it is possible to derive a function expressing a_{PbO} in terms of weight loss rate and physical and thermodynamic constants.

We have developed and refined this method for determining the equilibrium lead oxide activities and compared the results to standard, lead oxide systems for which reliable thermodynamic information is already available. An example is the equilibrium reaction

$$PbZrO_3(s) \longleftrightarrow PbO(g) + ZrO_2(s) \tag{4}$$
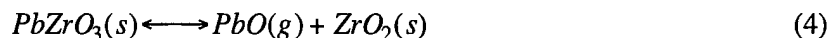
for which Knudsen cell effusion information was obtained between 850 and 1000 °C. Figure I.3 shows the weight loss rates at a series of temperatures and typifies the kind of information that is being collected on the PMNT system. The lead oxide activities so obtained compare quite well with published values that were obtained by electrochemical methods as shown in Fig. I.4, thus providing confidence in our methods. This agreement was due largely in part to our refinements in interpreting the gas phase thermodynamics and in interpreting Knudsen effusion cell kinetics.
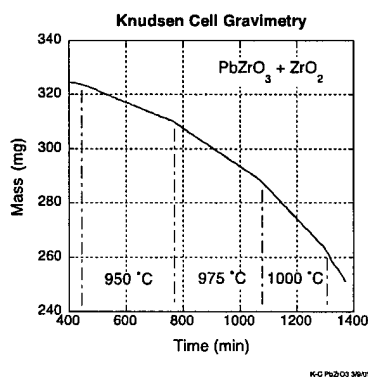

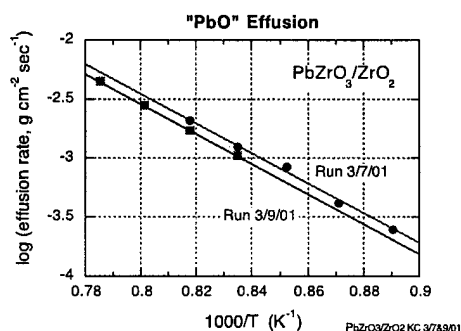Fig. I.3. Weight loss due to Knudsen effusion for PbZrO₃/ZrO₂ equilibrium for three different temperatures.

Fig. I.4. Comparison of temperature dependence of two different Knudsen effusion rates for PbZrO₃/ZrO₂ equilibrium.

References

(1)   Mangham, R. I. In *Chemistry and Biochemistry*; Arizona State University: Tempe, 2003, p 236.

(2)   Lucas, P.; Petuskey, W. T. *J. Am. Ceram. Soc.* **2001**, *84*, 2150-2152.

(3)   Drowart, J.; Colin, R.; Exsteen, G. *Trans. Faraday Soc.* **1965**, *61*, 1376-1383.

(4)   Hardtl, K. H.; Rau, H. *Solid State Communications* **1969**, *7*, 41-45.

(5)   Holman, R. L.; Fulrath, R. M. *Journal of The American Ceramic Society* **1972**, *55*, 192-195.

(6)   Holman, R. L.; Fulrath, R. M. *J. Appl. Phys.* **1973**, *44*, 5227-5236.

(7)   Cook, L. P.; Wong-Ng, W. In *Ceramic Transactions*; Wong-Ng, W., Holesinger, T., Riley, G., Guo, R., Eds.; American Ceramic Society: Westerville, Ohio, 2000; Vol. 104, pp 61-69.

(8)   Kazenas, E. K.; Petrov, A. A. *Izvestiya Rossiiskoi Akademii Nauk, Metally* **1996**, *4*, 22.27.

(9)   Knacke, O.; Richthofen, A. v. *Z. Physikalische Chemie* **1994**, *187*, 257-264.

(10)   Popovic, A.; Lesar, A.; Gucek, M.; Bencze, L. *Rapid Comm. Mass Spec.* **1997**, *11*, 459-468.